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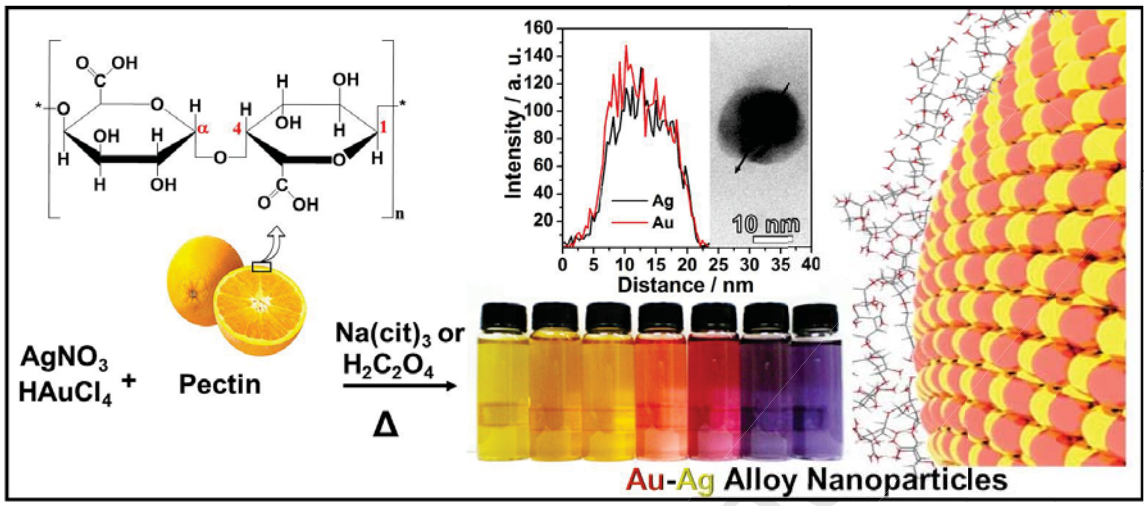
Sodium citrate, oxalic acid or pectin were used as reducing agents;

Colloids spanning all visible region were obtained depending on Ag/Au-ratio and pH;

Pectin is a highly efficient stabilizer of nanocolloidal solutions for years.

Graphical Abstract (GA)



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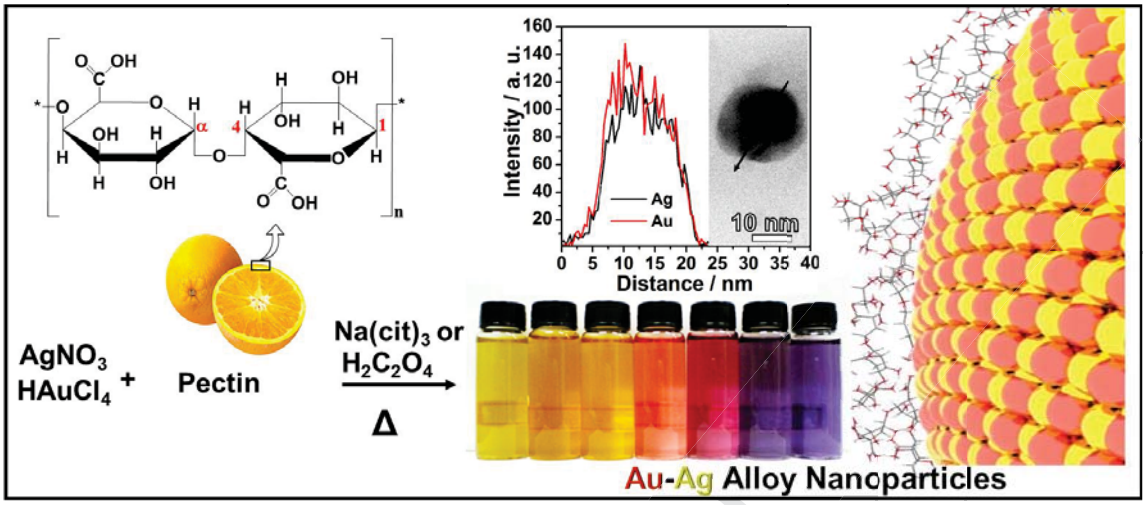
Abstract

The role of orange based pectin in the nucleation and growth of silver and gold nanoparticles is addressed. Pectin is a complex polysaccharide found in fruits such as oranges, lemons, passion fruits or apples. It displays smooth and hairy chain regions containing hydroxyl-, ester-, carboxylate- and eventually amine groups that can act as surface ligands interacting under various pH conditions more or less efficiently with growing nanometals. Here, a high methoxy pectin (> 50% esterified) was used as a stabilizer/reducing agent in the preparation of gold, silver and silver-gold nanoparticles. Commercial pectin (CP) and pectin extracted from orange bagasse (OP) were used. Optionally, trisodium citrate or oxalic acid we used to reduce $AgNO_3$ and $HAuCl_4$ in aqueous environment. Characterization methods included UV-VIS absorption spectroscopy, transmission electron microscopy, electron diffraction and energy-dispersive x-ray spectroscopy. The results show that under different pH conditions, pectin and reducing agents allow producing various nanostructures shapes (triangles, spheres, rods, octahedrons and decahedrons) often with high polydispersity and sizes ranging between 5 nm and 30 nm. In addition, depending on Ag/Au-ratio and pH, the surface plasmon bands can be continuously shifted between 410 nm and 600 nm. Finally, pectin seems to be a highly efficient stabilizer of the colloidal systems that show a remarkable stability and unchanged optical spectral response even after five years.

Keywords: gold, silver, nanoparticle, pectin.

Graphical Abstract (GA)



Highlights

Pectin from orange was used as stabilizer of Ag, Au and Ag-Au nanoparticles;

Sodium citrate, oxalic acid or pectin were used as reducing agents;

Colloids spanning all visible region were obtained depending on Ag/Au-ratio and pH;

Pectin is a highly efficient stabilizer of nanocolloidal solutions for years.

1. Introduction

Gold and silver nanoparticles find a range of applications including catalysis,[1] nonlinear optics,[2] opto-electronic devices,[3] sensing,[4] biomedical applications,[5] and others.[6] Among several interesting properties, single aqueous suspensions of Au and Ag nanoparticles exhibit fascinating colours. Due the collective oscillation of conducting electrons on the surface of those nanoparticles, strong coupling takes place with specific wavelengths of the incident light, which, in turn, results in absorption and scattering bands in visible region. This phenomenon is widely known as surface plasmon resonance (SPR). Aqueous suspensions of spherical Au and Ag NPs usually display strong SPR bands around 400 and 520 nm, respectively.[7] It is worth to pointing up that by tuning the size and shape of those NPs, the control over the optical properties becomes feasible and even predictable.[8] Owing the remarkable properties of Au and Ag nanoparticles, when these metals are combined at nanometric scale, yielding alloy Ag-Au compositions, rich and exciting properties can be improved than that of single metal. In fact, the absorption of Au-Ag alloy NPs can be tuned along the visible region by varying the alloy composition.[46]

Considering the several techniques used in the preparation of metals NPs since the pioneering work by Michael Faraday in the 19th century,[9] it may be noted that reduction of metal ions precursors in solution-phase remains the simplest and most versatile approach. The fundamental aspects of preparation and stabilization of Au nanoparticles was reviewed by Toma *et al*.[10] Particular emphasis has been placed on the use of sodium citrate as mild reducing agent in distinct methods such as

electrochemical,[11] sonochemical,[12] thermal[13] and photochemical[14] methods. To date, one of the most used solution-phase methods for the synthesis of spherical Au nanoparticles was developed by Turkevich *et al.*[15], which is based on the reduction of gold salts ($AuCl_3$ or $HAuCl_4$) in a boiling aqueous solution containing sodium citrate. Besides reducing agent, citrate ions can also play a role as capping agent by hindering the agglomeration among Au NPs, primarily due the electrostatic repulsion of carboxylate groups. Because the strong affinity between sulfur and gold, ligands displaying the thiol functional group have been extensively used as an effective capping agent of Au nanoparticles,[16] and may also perform controllable fashion on the surface properties of such nanoparticles.[17] In the case of the synthesis of Ag nanoparticles, strong reducing agents, such as borohydride[18], other than mild ones (i.e. ascorbic acid and citrate[19]) have been also employed in solution-phase methods. Several others methods have been proposed including microwave plasma synthesis,[20] electrolysis of Ag salts,[21] rapid expansion of supercritical solvents,[22] microemulsion,[23] photoreduction of Ag ions[24] and controlled synthesis in organic solutions.[25] Gold–silver alloy nanoparticles can be obtained by simple co-reduction of chlorauric acid and silver nitrate with sodium citrate in aqueous solutions.[46]

Green synthesis of nanoparticles are emerging as an alternative to physical and chemical methods.[26] These environmentally benign methods use micro-organisms,[27] enzymes,[28] plant extracts,[29] fruits or fruit peels[30] and fungi[31] that act as reducing agents as well as capping agents. In general, the colloidal stability is achieved through functionalization of the NPs surface, preventing agglomeration

either by electrostatic repulsion or steric hindrance. To this end, surfactants and polymers with donor atoms or specific chemical groups[32] are highly desirable to develop a reliable protective capping. For example, poly(vinylpyrrolidone) (PVP) is one of the most commonly neutral synthetic polymer studied as stabilizer in the synthesis of metallic nanoparticles.[33] The interaction between PVP molecule towards the metal atoms of the nanocrystal surface occurs through affinity of oxygen and nitrogen donor atoms present in the amide carbonyl group of PVP molecule. For instance, the large skeletal chain of PVP provide steric hindering against aggregation among the nanoparticles. Pectin and other heteropolymers from natural sources such as gum arabic,[34] carrageenan,[35] chitosan[36] and heparin[37] have also similar properties that allow them accomplish as reliable stabilizing agents for metal colloidal systems by forming a protective coating that prevents eventual precipitation.[38]

The condensation kinetics, shape tuning and long term stability of colloidal metal particles depends strongly on the geometry and chemistry of metal precursors, templating-, stabilising- as well as reducing agents and solvents. Pectin is a complex polysaccharide with smooth and hairy chain regions and is found in almost all plants. The main sources with commercial interest are the apple pomace, peel of citrus fruits and of passion fruit.[39] The composition of the pectin molecule depends on its source. For example, pectin from citrus fruits contains less neutral sugars and smaller molecular size compared with apple pectin.[40] Pectin has a complex structure (Figure 1) mainly composed of (1→4) linked α-D galacturonic acid esterified units. The acid groups along the chain are esterified with methoxyl

groups on natural materials. It presents a rate of 1-4% of L-rhamnose (Rha) units linked by α-(1 → 2) that interrupt the main chain.[41] Pectin chains contain hydroxyl-, ester-, carboxylate- and eventually amine groups that can act as surface ligands and interact under various pH conditions more or less efficiently with growing nanometals.

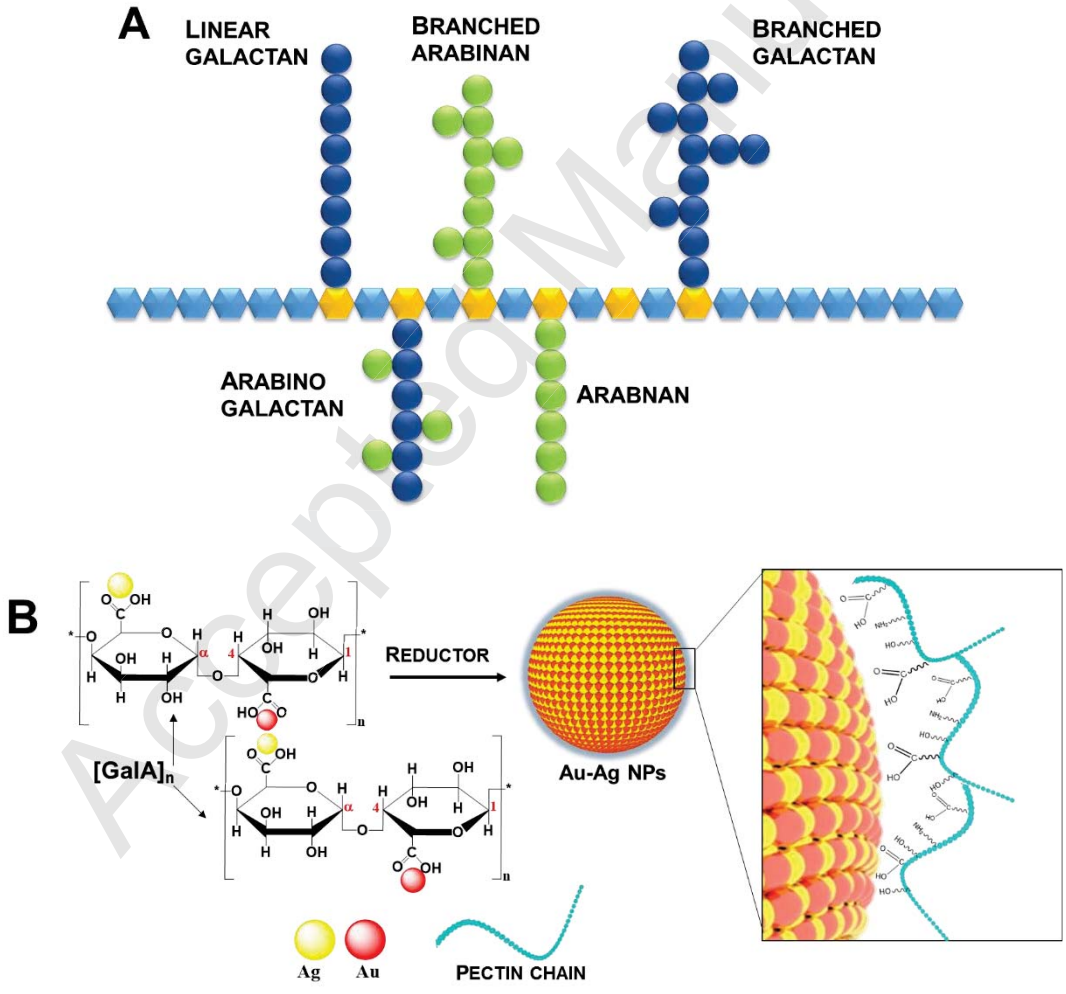


Figure 1. (A) Complex Pectin structure containing fragments of linear helical polysaccharide polymer consisting of α-1,4-linked D-polygalacturonic acid (GalA)

units, rahmnose disrupted hairy regions with the side chains containing other natural linear or branched sugar units (arabinose, galactose or arabinogalactose); (B) electron donor elements (oxygen or nitrogen) presented in carboxyl- hydroxyl-, ester-, as well as amido-functions groups, which present high affinity with Au^{3+} and Ag^{+} and minimize the chemical potential in order to stabilize Au-Ag alloy nanoparticles.

The presence of methoxyl groups and carboxyl groups in pectin is a favorable factor for using this material in some applications like the stabilization of colloids. The main goal of this work was to use Pectin extracted from orange bagasse presenting high esterification degree (76%) in the preparation of gold, silver and gold-silver nanoparticles. Several different properties can be envisaged and in a previous contribution, singlet oxygen generation in riboflavin water solutions was observed to be enhanced by pectin stabilized silver nanoparticles.[42]

2. Experimental

2.1 Reagents and apparatus

Commercial pectin (CP Kelco brand) type Genu 105 with esterification degree of 67% was used as a sample standard. $HAuCl_4$, $AgNO_3$, oxalic acid, trisodium citrate and methyl orange (Sigma Aldrich) were used.

The UV-VIS absorption spectra of the colloids were measured by using a Varian CARY 5 spectrophotometer. High resolution transmission electron microscopy (HRTEM) images and electron diffraction analysis were performed

using a HRT JEOL3010 URP equipment operating at 300 kV and a Philips CM 12 microscope equipped with a super-twin lens (C_s = 1.2 mm) and a 9800 EDX analyzer (Helmholtz Zentrum Berlin) being operated at 120 kV . Samples were prepared by placing a drop of nanoparticles suspension onto the surface of a Lacey formv/carb 300-mesh copper grid, followed by evaporation of the solvent. A field-emission gun transmission electron microscope (FEG-TEM) JEM 2100 operating at 200 kV and equipped with an energy dispersive x-ray spectroscopy (EDS) detector was used to map a single particle of gold and silver.

2.2 Extraction of pectin from oranges

Pectin was extracted from the mesocarp of oranges under acid hydrolysis. The triturated orange mesocarp was heated in water (70 °C) for 10 minutes to inactivate endogenous cell wall degrading enzymes, such as poly(galactorunase). The solid was separated and then dried in a ventilated oven at 35 °C.

The dried raw-material was suspended in distilled water (solid-liquid ratio 1:10, w/v) and HCl 0.1 M solution was added to adjust the pH between 1.5-3.0. The mixture was continuously stirred at 60 °C for two hours ant then filtered. Ethanol was added to the filtrate in order to precipitate the pectin. The precipitate was dried by lyophilization.

The esterification degree (ED) of orange pectin (OP) was determined by potentiometric and conductometric titration based on the method described by Bochek *et al*.[43] In a first step, an aqueous solution of OP 0.05% w/w was titrated with NaOH 5mM to determine the number of free carboxy groups of

poly(galacturonic) acid. Once determined the free carboxy groups, NaOH solution (40 ml) was added to the pectin solution in order to saponify the methyl ester groups of the polymer. Afterwards, excess of NaOH was titrated with HCl 5mM. The total number of the carboxyl groups is equal to the sum of the free and esterified groups. The ED is given by the ratio between the content of carboxylic groups esterified and total.

2.3 Preparation of silver, gold and gold-silver nanoparticles

The following solutions were prepared: $HAuCl_4$ 1mM and $AgNO_3$ 1mM. Pectin extracted from orange (OP) and commercial pectin were used to prepare the nanoparticles under the same conditions. An aqueous solution of pectin 0.5% (w/v) was prepared under stirring for two hours at 40 ºC. Solutions of sodium citrate 0.1 M and oxalic acid 0.1 M were prepared as reduction agents.

2.3.1 Gold nanoparticles

In a typical synthesis, OP (1 mL) and $HAuCl_4$ (3mL) solutions were added to distilled water (25 mL) under stirring. The resulting solution was heated at 80 ºC, and the reducing agent (1 mL of trisodium citrate or oxalic acid solutions) was added. The solution was kept boiling until colour change, then the heat source was immediately removed. In a second procedure the pH of the resulting solution was set to 11 by adding solution of NaOH 0.1 M. Afterwards, it was heated up to 80 ºC under vigorous stirring and oxalic acid solution (1 mL) was introduced. The

solution was kept boiling until colour change, then immediately removed from the heat.

2.3.2 Silver nanoparticles

Silver nanoparticles were prepared with a similar methodology used for the synthesis of gold nanoparticles mentioned before. Only trisodium citrate was used as reducing agent.

2.3.3 Pectin as reduction agent of gold

OP could be used as reducing and stabilizer agent of Au NPs. OP (3 mL) and $HAuCl_4$ (3 mL) solutions were added to distilled water (24 mL) under stirring. The solution was kept boiling until colour change, then immediately removed from the heat. On the course of the reaction, several colours changing took place on the aqueous solutions, whose characteristic extinction bands were carefully monitored by UV-Vis spectrophotometry.

2.3.4 Au-Ag alloy nanoparticles

Au-Ag alloy nanoparticles were prepared by modifying the Ag:Au molar ratio. In this case, only trisodium citrate was used as reduction agent. The solutions of OP (1 mL), $AgNO_3$ and $HAuCl_4$, whose Ag:Au volume ratio was set to 3:1, 1:1 or 1:3, were added to distilled water. The final volume was 30 mL. They were heated at 80 ºC and trisodium citrate solution (1 mL) was added. The solution was kept boiling until colour change, then immediately removed from the heat.

The different routes used for the preparation of colloidal systems are presented in Figure 2.

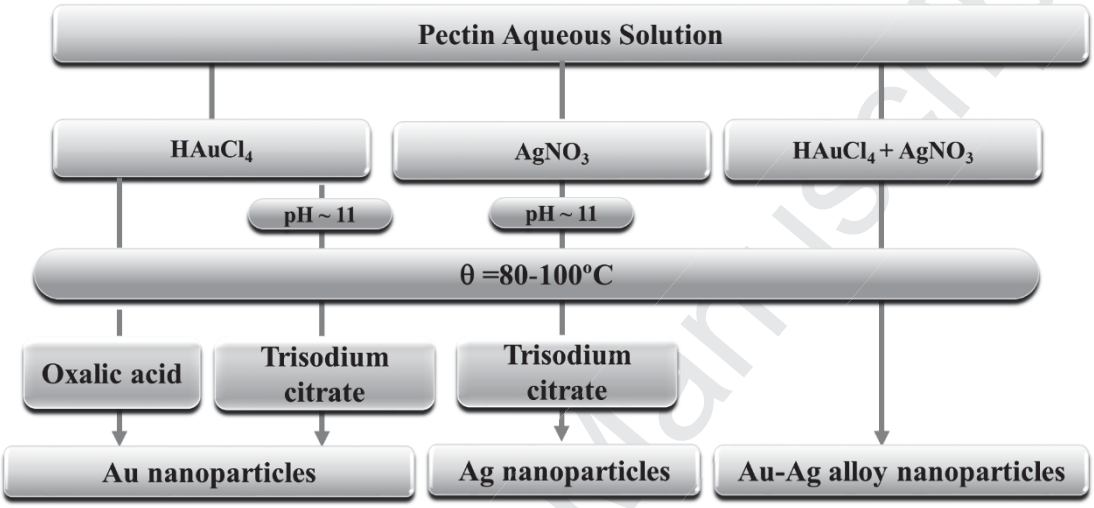


Figure 2. Schematic illustration of the synthesis of Au, Ag and Ag-Au alloy nanoparticles.

3. Results and discussion

The pectin extracted from orange was characterized by potentiometric and conductometric titrations to determine the esterification degree (ED) of poly(galacturonic) acid. The equivalence point was determined from the titration curves shown at Figure 3. Pectin was obtained with ED of 76 %. The isoelectric point (IEP) was located around pH 5, implying that below this pH the polymer chains are positively charged and strongly interacting with the nanoparticles. On the other hand, above pH 5 the negatively charged chains act as steric stabilizers

and exhibit an electrostatic repulsion towards negatively charged condensing nanoparticles. Thus, this situation favours the growth of particles with larger sizes.

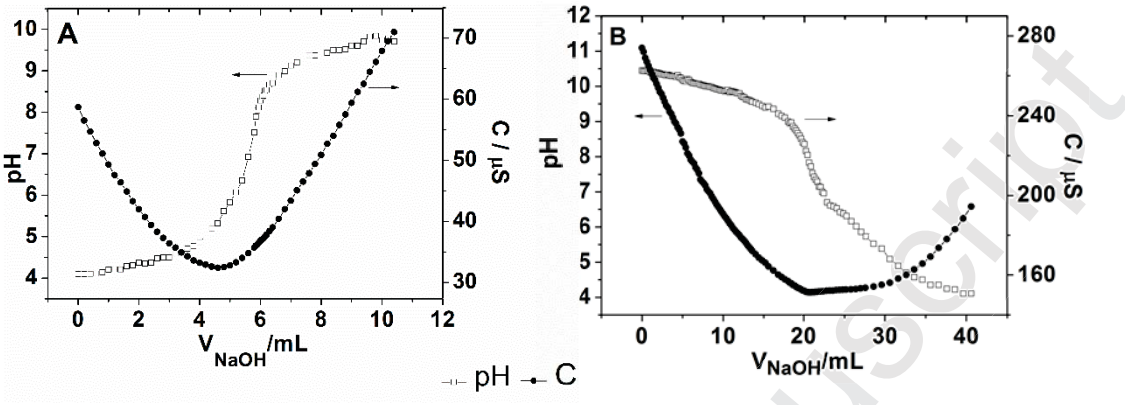


Figure 3. Potentiometric and conductometric titration curves collected on aqueous OP solution (0.05% w/w); (A) Titration of free carboxy groups using NaOH 5 mM. (B) Back titration with HCl 5mM after saponification of methyl ester groups.

The optical properties of gold and silver nanoparticles depend strongly on their size and shape. It is well known that resonance of the incident light with surface plasmons is the main mechanism for the appearance of colours. Aqueous suspensions of Au NPs are red for nanoparticles in the range between 2 and 10 nm. They display violet colour for larger sizes of nanoparticles.[44] In fact, the formation of nanoparticles in solution can be easily followed by using UV-VIS-NIR spectroscopy.[45]

The products obtained in this work displaying different colours are pictured in Figure 4. The samples form translucent solution with yellowish colour for aqueous suspension of Ag NPs (a) Au-Ag alloy NPs with molar ratio 1:3 (b) and Au-Ag alloy NPs in equimolar concentrations (c). A reddish aqueous solution were found for Au NPs reduced by trisodium citrate with particle size between 2 and 10 nm (d)

and Au NPs reduced by OP (e). Finally, a violet translucent solution is obtained for Au NPs reduced by oxalic acid (f, g) at distinct pH (2.46 and 3.18 respectively). In this case, NaOH was added before the introduction of the reducing agent where such violet colour indicated that Au NPs so-obtained are larger than 10 nm. It is to be noticed that the aqueous suspension of Au NPs obtained by using trisodium citrate (pH = 6.25) as reducing agent showed a different colour compared to the solution obtained by using oxalic acid (pH = 2.46) as a reducing agent.

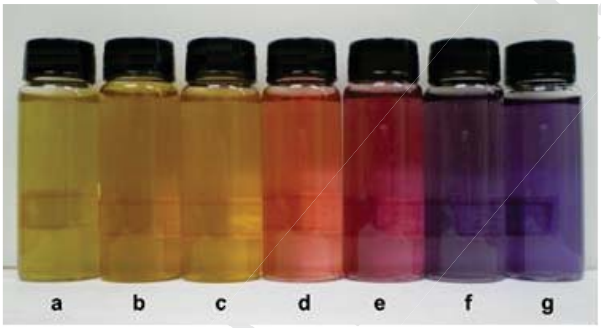


Figure 4. Different colours of aqueous solutions obtained for Ag NPs (a), Ag-Au 3:1 NPs (b), Ag-Au 1:1 NPs (c), Au NPs reduced by trisodium citrate (d), Au NPs reduced by pectin (e), Au NPs reduced by oxalic acid and, (f) Au NPs reduced by oxalic acid in alkaline medium(g).

A control sample containing Au NPs prepared in the absence of pectin was violet in colour, but the system showed up not stable. Aggregation of particles was observed around 30 minutes after the introduction of reducing agent mostly due to the lack of a stabilizing agent.

Figure 5a shows UV-VIS spectra. Ag NPs suspension showed a characteristic peak at 409 nm. Absorption spectra of Au NPs showed a broad band centered at 522 nm for samples prepared with trisodium citrate as reducing agent. For samples

prepared with oxalic acid, the absorption maximum was observed to depend on the pH (540 to 570 nm).

Au-Ag alloys particles are formed in preparations where Au and Ag ions are reduced simultaneously by trisodium citrate in the same solution. The alloy formation is confirmed from the fact that the optical absorption spectra show only one plasmon band.[46] Two bands would be expected for the case of a mixture of single gold and silver nanoparticles,[47] or Au@Ag core-shell nanoparticles.[48] There is a shift of the peaks along the wavelength according to the changing concentrations of silver and/or gold. A linear dependence of the plasmon absorption maximum on the composition of the nanoparticles is shown in Figure 5b.

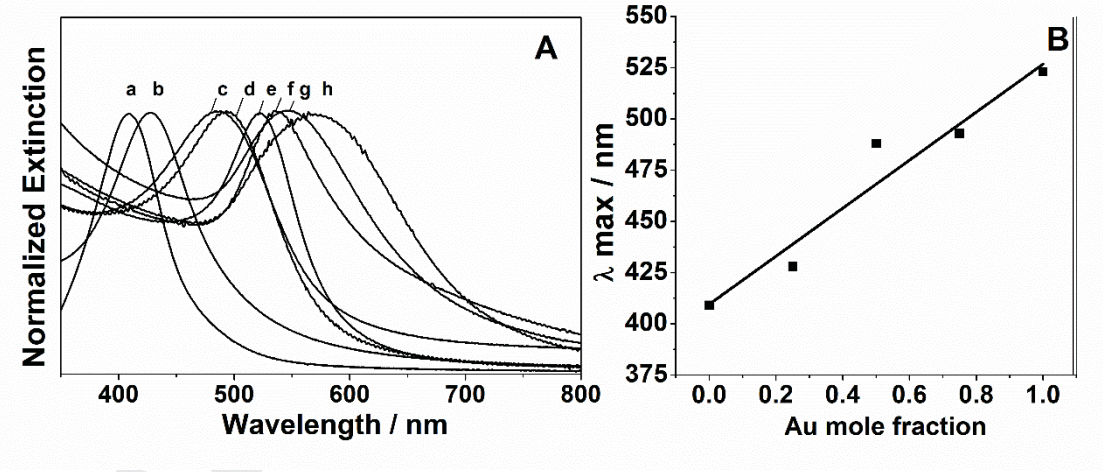


Figure 5. (A) Extinction spectra recorded from aqueous solution of Ag NPs (a), Ag-Au 3:1 NPs (b), Ag-Au 1:1 NPs (c), Ag-Au 1:3 alloy NPs (d), Au NPs reduced by trisodium citrate (e), Au NPs reduced by oxalic acid (f), Au NPs reduced by OP (g), Au NPs reduced by oxalic acid at alkaline medium (h). (B) Plot of the wavelength corresponding to the maximum extinction intensity as function of the

mole fraction of Au for nanoparticles produced by using trisodium citrate as reducing agent.

Increasing particle size and/or aggregation usually leads to red shift and broadening of the plasmon band. These effects can be ruled out with aging of the suspensions prepared here, as may be observed in the UV-Vis spectra (Figure 6). In fact colloidal suspensions remained stable from the time of preparation of the solutions up to five years. Moreover, it is worth to outline that Au NPs prepared in the presence of OP showed the same optical and morphological characteristics of those prepared with commercial pectin.

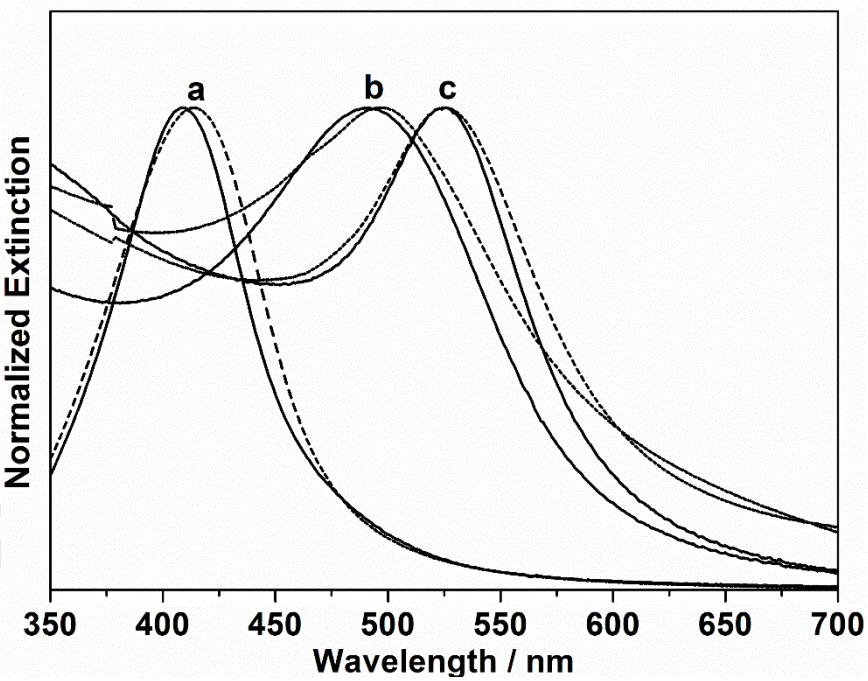


Figure 6. Extinction spectra recorded from aqueous solution at the time of preparation (straight line) and after five years (dashed line) for Ag (a), Ag-Au 1:1 (b) and Au NPs (c).

TEM images, shown in Figure 7 indicate that Au and alloyed Ag:Au alloy NPs were successfully obtained. The use of different reducing agents allowed the fabrication of various nanostructures shapes (triangles, spheres, rods, octahedrons and decahedrons) and sizes (5 nm - 30 nm).

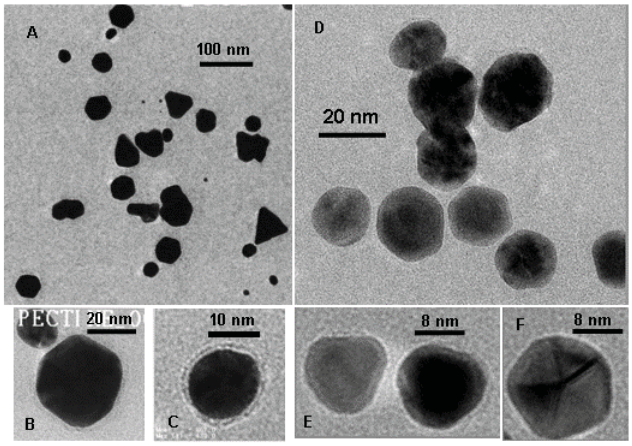


Figure 7. TEM images of OP capped Au NPs (A, B, C) and alloyed Ag:Au = 1:1 nanostructures (D, E, F) with clearly visible pectin stabilizer shells.

Figure 8 shows TEM images obtained for Au and Ag-Au alloy NPs prepared with trisodium citrate as reducing agent and their corresponding size distribution. The nanoparticles showed quasi-spherical shape. Ag and Ag-Au alloy NPs exhibited mean diameters ranging from 13-15 nm while Au NPs showed larger diameters (i.e. 24 nm).

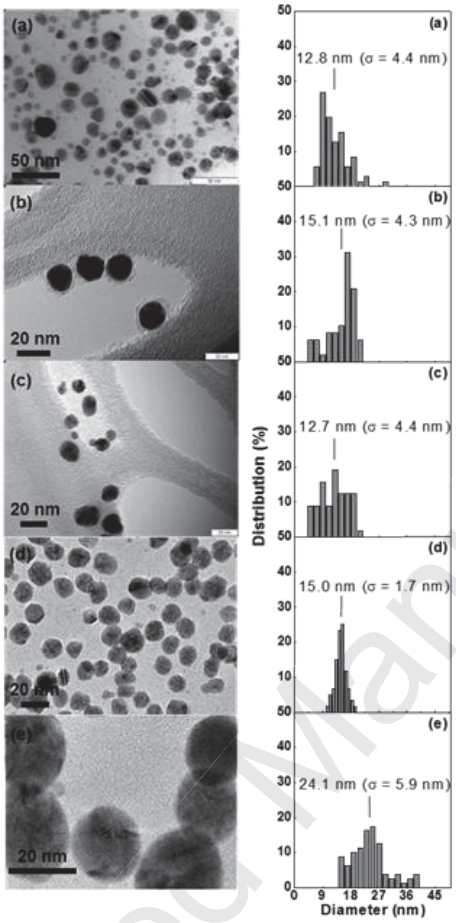


Figure 8. TEM images and size distributions of the following NPs: Ag (a), Ag-Au 3:1 (b), Ag-Au 1:1 (c), Ag-Au 1:3 (d), Au reduced by trisodium citrate (e).

Figure 9 shows TEM images and size distribution of nanoparticles prepared using OP or oxalic acid as reducing agent. Besides spheres, other morphologies like prisms could be observed. Mean sizes of particles were found to be 14 and 20 nm for particles reduced by OP or oxalic acid, respectively.

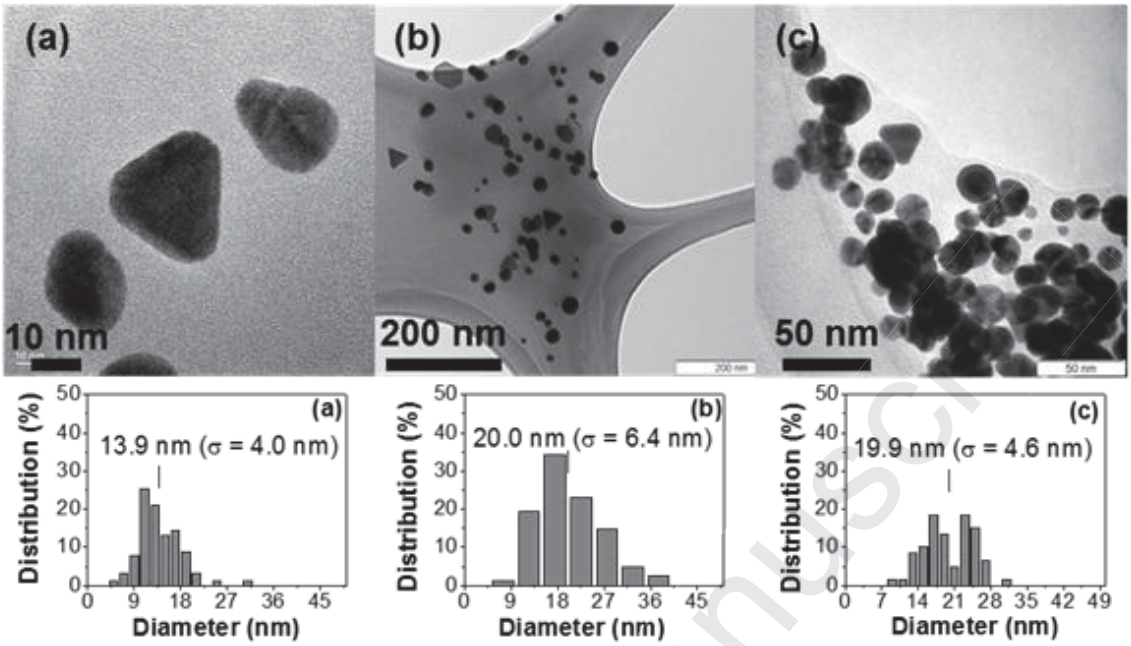


Figure 9. TEM images and size distributions of Au NPs reduced by pectin (A), oxalic acid (B) and oxalic acid under alkaline conditions (C).

Electron diffraction analysis was performed to determine the structure of the particles (Figure 10). Electron diffraction pattern for Au NPs reduced by trisodium citrate (Figure 10a) presented interplanar spacings of 0.2353 nm, 0.2025 nm, 0.1446 nm and 0.1234 nm. For the Ag-Au 1:1 and Ag-Au 1:3 alloy NPs (Figures 10b and 10c), the interplanar spacings were 0.2350 nm, 0.2038 nm, 0.1450 nm and 0.1230 nm. In all cases, the calculated interplanar spacings corresponded to the (111), (200), (220) and (113) planes that confirm a face-centred cubic structure of pure Au NPs reduced by trisodium citrate and alloyed Ag-Au alloy NPs.[49]

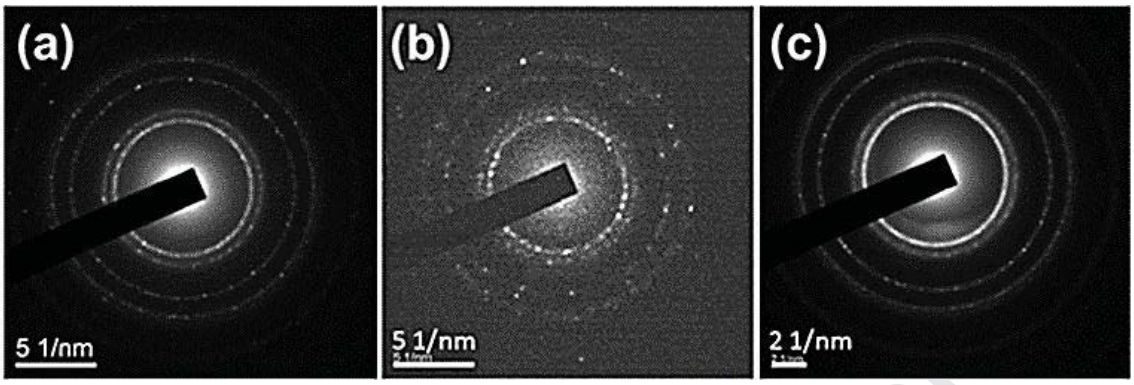


Figure 10. Electron diffraction pattern of Au NPs reduced by trisodium citrate (A), Ag–Au alloy NPs with molar ratios 1:1 (B) and 1:3 (C).

Energy-dispersive x-ray spectroscopy (EDS) was used to map a single alloy particle (Ag–Au 1:1). The particle was scanned across the line indicated on Figure 11(a) and the EDS spectrum was recorded at each probe position. Figure 11(b) shows the elemental mappings of gold and silver constructed from those spectra, whose EDS elemental intensity profiles (vertical axis) of Ag (red) and Au (green) were plotted against the line scan probe position (horizontal axis). The similar intensity along the line for elemental mappings of Au and Ag suggest the homogeneous formation of Ag-Au alloy NPs with molar ratio of 1:1. The EDS spectrum shown in Figure 11(c) was obtained at the position of 16 nm. (Cu and Fe lines are due to contamination of the experimental set-up)

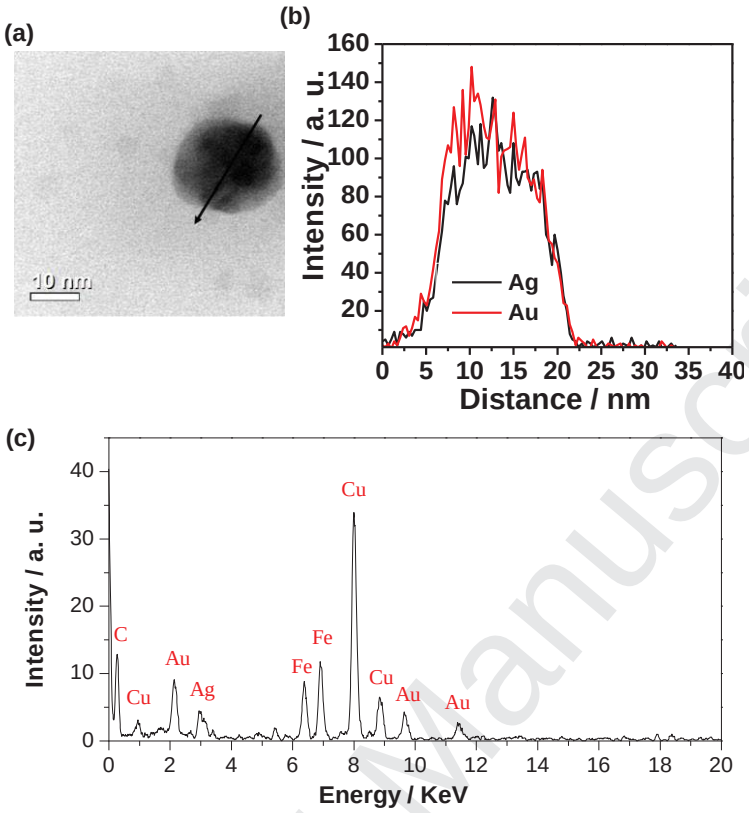


Figure 11. TEM image of a bimetallic nanoparticle (Ag–Au 1:1) and the line indicating the region and direction analysed by EDS (a); the corresponding chemical mapping of Ag (red) and Au (green) constructed from EDS line (b) EDS spectrum obtained at the position of 16 nm (c). (Fe and Cu lines are instrumental artifacts)

4. Conclusions

In this contribution, the role of orange based pectin in the nucleation and growth of silver and gold nanoparticles was addressed. The conditions for the preparation of Au-Ag colloids with different colours spanning the entire visible range by using pectin as a stabilizer were well determined. Nanocolloids so prepared were

observed to be stable for years remain stable with the same colour and no aggregation.

The formation of Ag-Au alloy nanoparticles is supported by the TEM-EDS results, and also by the absorption spectra presenting only one plasmon absorption band, the shift of the band proportional to the metal molar ratio and the absence of a core-shell structure on TEM images.

Acknowledgements

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